Technical Paper 381

DEPARTMENT OF COMMERCE
HERBERT HOOVER, SECRETARY
BUREAU OF MINES
SCOTT TURNER, DIRECTOR

HEAVY LIQUIDS FOR MINERALOGICAL ANALYSES

BY

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HEAVY LIQUIDS FOR MINERALOGICAL ANALYSES

By JOHN D. SULLIVAN

INTRODUCTION

In the course of its work for the advancement of efficiency in the mineral industries the Bureau of Mines has studied gravity methods of concentrating ores and of separating the valuable minerals from the worthless gangue by the use of jigs, tables, or classifiers. These studies have involved the microscopic examination of ores and the making of mineralogical analyses in order to determine the different minerals present, the fineness of the mineral grains, and the distribution of these grains through the mass of an ore.

The purpose of the investigation described in this paper was to develop a series of heavy liquids for use in mineralogical analyses—to get a series of cheap liquids that would enable one to separate by means of the sink-and-float method the heavier mineral particles from the gangue and, if possible, to separate the various minerals from one another. The investigation has consisted largely in a study of the liquids already in use and the development of suitable liquids other than those.

ACKNOWLEDGMENTS

The author wishes to thank O. C. Ralston, assistant chief metallurgist, and C. G. Maier, associate metallurgist, Pacific experiment station, Bureau of Mines, for their helpful suggestions and their assistance.

ESSENTIAL PROPERTIES OF LIQUIDS FOR MINERALOGICAL ANALYSES

Specific gravity is by far the most important of the physical properties on which mechanical methods of separating minerals depend. The so-called heavy liquids are used to isolate rock components according to their specific gravity. A given specimen of rock may contain gangue with a gravity of 2.5 and sulphides with a gravity of 5.0. If a liquid of a gravity of 3.5 is taken, the rock powder immersed in the liquid, and the resulting mixture well shaken and allowed to stand, the heavier particles of sulphide sink to the bottom while the lighter particles of gangue float to the top. If the pure powder of two different minerals is well mixed, a quantitative separation of each component may be made by using a liquid whose specific gravity is about the mean between the powders. In rocks

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the relations are not so simple, however, as the particles rarely consist of only one mineral, but generally consist of several minerals intergrown in different proportions. The separation must be carried out in single stages in order to separate the pure minerals from combinations resulting from such intergrowth. Samples finer than 50 to 60 mesh are often unsatisfactory for separation by the sink-and-float method. If the particles are much finer, separation takes place very slowly; if the particles are as fine as dust, there may be no separation whatever, because the particles remain suspended in the liquid, especially if that is immobile. H. E. Messmore, of the Bureau of Mines, in a letter to the author reports that in working with spars he has found it possible successfully to separate various samples of which 40 per cent were finer than 325 mesh and all of which went through 48 mesh.

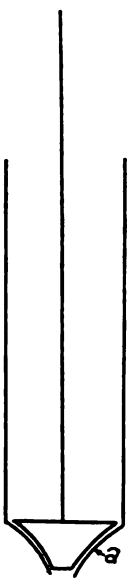

FIGURE 1.—Apparatus for separating "sink" from "float": *a*, Ground glass

The mobility of the liquid has much to do with the speed and accuracy of the separation. Most heavy organic liquids are usually quite mobile, whereas molten inorganic salts are less mobile and sometimes are very immobile. To be of value in making specific gravity separations a liquid should be capable of being easily concentrated or diluted, so that every gradation of specific gravity can be obtained. In addition, the solutions obtained should be colorless or at least transparent.

METHOD OF SEPARATION

The separation itself consists essentially in weighing the specimen to be separated, shaking it with an excess of a satisfactory separating liquid, and allowing it to stand. The material lighter than the liquid will float; that heavier will sink.

The separation can be carried out in any suitable vessel. The size of the vessel will depend on the amount of material to be separated and the amount of heavy liquid available. A separatory funnel is frequently used, because after the separation the stopcock can be turned, and the heavier particles which have sunk to the bottom can be drained off. Then the lighter particles which have floated can be poured or drained off. Bird and Messmore [1] have described a method using a 2-liter bottle and siphon for the separation of coal by means of heavy organic liquids.

Penfield [2] has described a method of separation where small quantities are employed. He uses (see fig. 1) a glass tube with a ground-glass stopper at the bottom. To the stopper is connected a glass rod

[1] Bird, B. M., and Messmore, H. E., The Float-and-Sink Test for Fine Coals: Reports of Investigations, Serial 2586, Bureau of Mines, March, 1924.

[2] Penfield, S. L., "On some devices for the separation of minerals of high specific gravity": Am. Jour. Sci., vol. 50, ser. 3, No. 300, 1895, p. 446.

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longer than the tube itself. After the rock particles have separated, the glass stopper is moved up enough to permit the heavier particles and liquid to run out. When enough liquid has run out, the glass stopper can be replaced. In this way the "sink" can be separated from the "float." When molten salts are used, a hard-glass test tube of suitable size is very satisfactory. After the separation has taken place, the melt can be cooled by immersion in cold water, the tube cut into sections, and the separated components recovered by dissolving away the solidified separating medium.

McMillan and Bird [3] have described an apparatus for float-and-sink tests of coarse sizes of coal.

SPECIFIC GRAVITIES OF SOME COMMON MINERALS

A table of specific gravities of some of the more common minerals is given below to make plain the specific gravity requirements of the heavy liquids.

TABLE 1.—*Specific gravity of some common minerals*

Mineral	Specific gravity	Mineral	Specific gravity
Feldspars	2.55–2.75	Barite	4.3 –4.6
Quartz	2.6 –2.66	Pyrrhotite	4.5 –4.6
Calcite	2.71–2.72	Pyrite	4.5 –4.6
Biotite	2.7 –3.1	Stibnite	4.52–4.62
Dolomite	2.8 –2.9	Ilmenite	4.5 –5.0
Realgar or orpiment	3.4 –3.6	Magnetite	4.9 –5.2
Rhodocrosite	3.5 –4.5	Bornite	4.9 –5.4
Siderite	3.83–3.88	Chalcocite	5.5 –5.8
Sphalerite	3.9 –4.1	Cobaltite	6.0 –6.1
Corundum	3.95–4.11	Arsenopyrite	6.0 –6.2
Chalcopyrite	4.1 –4.3	Wulfenite	6.7 –7.0
Rutile	4.15–4.25	Galena	7.4 –7.6
Chromite	4.3 –4.6	Cinnabar	8.0 –8.2

DETERMINATION OF SPECIFIC GRAVITY OF LIQUIDS

Hydrometer.—Several methods of determining the specific gravity of liquids are available. Use of a hydrometer is probably the quickest and easiest method if great accuracy is not required. The ordinary hydrometer, however, is not made to read high gravities, its upper range usually not exceeding 2.0. Although hydrometers giving a higher range of gravity than this can be purchased, they are rather expensive, as they have to be specially made. A person with ordinary skill in glass blowing can make his own heavy-liquid hydrometer and calibrate it himself. In purchasing or making a hydrometer the size must be taken into consideration. In work with heavy liquids usually a very small quantity of liquid is at hand, so use of a short, small hydrometer is essential. At its best a hydrometer requires a considerable volume of liquid.

[3] McMillan, E. R., and Bird, B. M., Coal-Washing Problems of the Pacific Northwest: Univ. Washington Eng. Exp. Sta., Bull. 28, 1924, 234 pp.

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Westphal balance.—Another and quite satisfactory method of determining specific gravity is by use of a Westphal balance. Usually the plummet accompanying the balance is capable of reading gravities only to 2.5, but a plummet can be made in the laboratory with which the specific gravity of any solution can be read. If the plummet is small enough, no large quantity of liquid is required. The Westphal balance is much more accurate than the hydrometer and costs only about $25.

Buoyancy of liquid.—A decidedly satisfactory method for a liquid that is molten at ordinary temperatures is to measure the buoyancy of the liquid. Two cubic centimeters of the liquid is usually enough. A piece of metal, such as platinum (or any other inert metal), is extended by a fine wire. This piece of metal is weighed in air and in

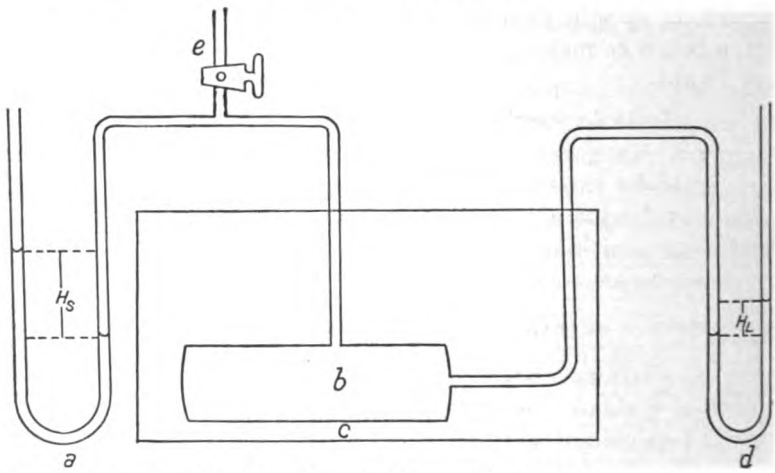

FIGURE 2.—Apparatus for determining specific gravity of liquids: *a*, Standard liquid; *b*, equalizing chamber; *c*, water reservoir; *d*, liquid being tested; *e*, to suction or pressure

the liquid; from the two weighings the buoyancy, and hence the specific gravity of the liquid, is determined.

Comparison of column of liquid.—Another method used in this investigation, and one suitable for use at high temperatures, was the measurement of the height of a column of the liquid which was exactly compensated by a given height of a liquid of known specific gravity. Water (specific gravity, 1) was chosen as the standard liquid, because in measuring liquids having a specific gravity of about 4, the height of the water column would be about four times the height of the column of the liquid whose specific gravity was being determined. The heights of the two liquid columns were determined with a cathetometer. Figure 2 illustrates the method. The purpose of the equalizing chamber shown is to furnish a sufficiently large volume, so that the pressure produced by small temperature changes

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in the U-tubes will not cause fluctuations in the heights of the liquids in the U-tubes.

Pycnometer.—Use of the pycnometer is the most accurate method of determining the specific gravity of a liquid, but as it is slow and cumbersome it is not recommended where other methods will suffice.

Many articles and books suggest the determination of specific gravity by adding minerals of known specific gravity until by observing whether they sink or float the specific gravity of the liquid is taken as that of a mineral particle which is just on the border line between sinking and floating. Such a method obviously can not be satisfactory. The specific gravity of the mineral particles must be accurately determined, because small admixtures of gangue or of a heavier component may cause the specific gravity to be quite different from that of the "pure" mineral. Moreover, it is well known that under suitable conditions a dry or greased needle can be made to float on water, unless stirring is used to break the air film on the surface of the needle. The surface tensions and the viscosity effects of molten baths, especially inorganic, may be sufficient to float a mineral which actually has a specific gravity considerably higher than that of the liquid. This is the method now ordinarily used to determine specific gravities of some of the heavier liquids, and its use accounts for some of the conflicting statements in the literature. For the same reason some investigators have concluded that they have obtained specific gravities which they never actually obtained. The specific gravity a solution must have to sink or float a mineral particle of a given specific gravity is discussed more in detail later in this paper.

HISTORICAL REVIEW

Two general classes of heavy liquids are discussed here—organic and inorganic. The two organic liquids most commonly used are bromoform, first suggested by van der Kolk,[4] with a specific gravity of 2.88, and acetylene tetrabromide ($C_2H_2Br_4$), suggested by Muthmann,[5] which has a specific gravity of 2.96. Brauns[6] used methylene iodide, whose specific gravity is 3.32 at 16° C.; this substance decomposes quite readily, however, even under the action of light. Messmore found that the discoloration caused by the decomposition can be removed by metallic copper, or by shaking for an instant in a flask with an aqueous solution of caustic soda.

[4] van der Kolk, J. L. C. Schroeder, "Beitrag zur Kartirung der quartären Sande": Neues Jahrb. Mineral., Geol., u. Paleont., Bd. 1, 1895, pp. 272–276.

[5] Muthmann, W., "Ueber eine zur Trennung von Mineralgemischen geeignete schwere Flüssigkeit"; Ztschr. Kryst. Mineral., Bd. 30, 1899. pp. 73–74.

[6] Brauns, R., "Ueber die Verwendbarkeit des Methylenjodids bei petrographischen und optischen Untersuchungen": Neues Jahrb. Mineral., Geol., u. Paleont., Bd. 2, 1886, pp. 72–78.

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Acid mercuric nitrate (specific gravity, 3.3 to 3.4) has been suggested by Schaffgotsch,[7] but it is unsatisfactory because its acidic properties have a destructive effect on many minerals.

The Sonstadt[8] or Thoulet[9] solution ($HgI_2.2\ KI$) has a specific gravity of 3.2. When NaI or LiI are used in place of the KI, the solution is known as the Duboin solution. This reagent can be diluted to any extent with water and be again concentrated by evaporation. A small excess of KI is permissible, but an excess of HgI_2 causes a precipitation due to hydrolysis when water is added.

Cadmium borotungstate, the Klein[10] solution—$9WO_3.B_2O_3.2Cd(OH)_2.16H_2O$), has a specific gravity of 3.36. It is decidedly viscous but can be mixed with water in all proportions without decomposition, and its mobility increases rapidly with dilution. It is decomposed by carbonates and metals. The most serious objection to this reagent is the difficulty of preparing it. W. B. D. Edwards[11] has described a method of preparation.

Barium mercuric nitrate, Rohrbach's solution,[12] is mobile and has a specific gravity of 3.59. It decomposes rapidly, and the concentrated solution can not be diluted with water. The method of diluting a concentrated solution is to add carefully to the concentrated solution a less concentrated solution in a thin layer and allow the two to diffuse.

A number of liquids have been described by Retgers.[13] He described thallium silver nitrate ($TlNO_3.AgNO_3$), which melts at about 75° C. to a mobile liquid having a specific gravity of about 4.6. H. E. Merwin, of the geophysical laboratory, states that in roughly equivalent proportions the specific gravity is about 4.5 at 75° C., and that $3AgNO_3.4TlNO_3$ melts at 100° C. and has a speci-

[7] Schaffgotsch, F. G., "Ermittelung des Eigengewichts fester Körper durch Schweben": Poggendorff's Ann., Bd. 116, 1862, pp. 279–289.

[8] Sonstadt, E., "Note on a new method of taking specific gravities, adapted for special cases": Chem. News, vol. 29, 1874, pp. 127–128.

[9] Thoulet, M., "Séparation des éléments non ferrugineux des roches fondée sur leur différence de poids spécifique"; Compt. rend., t. 86, 1878, pp. 454–456.

[10] Klein, M. D., "Sur la séparation mécanique par voie humide des minéraux de densité inférieure à 3. 6": Soc. française mineral., Bull. 6, vol. 4, 1881, pp. 149–155.

[11] Edwards, W. B. D., "On the preparation of a cheap heavy liquid for the separation of minerals": Geol. Mag., vol. 8, decade 3, 1891, p. 273.

[12] Rohrbach, Carl, "Ueber eine neue Flüssigkeit von hohem specifischen Gewicht, hohem Brechungsexponenten und grosser Dispersion": Ann. physik. Chem., Bd. 20, N. F., 1883, pp. 169–174.

[13] Retgers, J. W., "Ueber schewere Flüssigkeiten zur Trennung von Mineralien": Neues Jahrb. Mineral., Geol., u. Paleont., Bd. 2, 1889, pp. 185–92; "Versuche zur Darstellung neuer schwerer Flüssigkeiten zur Mineraltrennung. I. Die Acetate der Schwermetalle als schwere Schmelzen": Neues Jahrb. Mineral., Geol., u. Paleont., Bd. 1, 1896, pp. 212–221; "Versuche zur Darstellung neuer schwerer Flüssigkeiten zur Mineraltrennung. II. Die Nitrate und Doppelnitrate der Schwermetalle als schwere Schmelzen": Neues Jahrb. Mineral., Geol., u. Paleont., Bd. 2, 1896, pp. 183–195; "Die Bestimmung des spezifischen Gewichts von in Wasser löslichen Salzen. III. Die Darstellung neuer schwerer Flüssigkeiten": Ztschr. physik. Chem., Bd. 11, 1893, pp. 328–344.

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fic gravity of 4.68. Johannsen[14] says that Retgers found the specific gravity of $1AgNO_3.2TlNO_3$ is 4.8 and its melting point above 150° C.; $1AgNO_3.4TlNO_3$, specific gravity 4.85 and melting point about 200° C.; whereas pure $TlNO_3$ melts at 205° C. and has a specific gravity of 4.94. The double salt is decomposed by sulphides.

Holmes[15] and Weinshenck[16] state that $HgNO_3.1H_2O$ melts at 70° C. and has a specific gravity of 4.3.

Holmes says that thallous mercurous nitrate fuses at 76° C. and has a specific gravity of 5.3. Although it is rather unstable and decomposes near the boiling point of water, it may be useful where sulphides are present, as they do not decompose it. This melt is discussed in more detail later in this paper.

Clerici[17] has investigated numerous thallium salts of the organic acids and found thallium formate to be the one best adapted for a heavy solution. Aqueous solutions of this salt are colorless and nearly as free flowing as water. Both the solubility and gravity increase rapidly with increasing temperature. The amount of the salt necessary to prepare a saturated solution depends on the temperature. The specific gravity of the saturated solution, according to Clerici, is as follows:

Specific gravity of thallium formate at different temperatures

Temperature at °C.	Specific gravity	Temperature at °C.	Specific gravity
−10	2.58	50	4.11
0	2.86	60	4.32
10	3.14	70	4.50
20	3.40	80	4.67
30	3.64	90	4.76
40	3.87		

Clerici states that the salt melts at 95° C. and that the molten salt will float illmenite (specific gravity a little less than 5). He obtained no satisfactory results by combining the thallous formate with varying proportions of thallium and lead acetates, but mixtures of the formate with glycolate, malonate, maleate, succinate, or malate of thallium and a little water gave solutions having higher specific gravities than that of the formate alone at the same temperature. The malonate mixture (10 parts formate, 10 parts malonate, 1 part water) gave the best result. This mixture is odorless, colorless or

[14] Johannsen, Albert, Manual of Petrographic Methods. New York, 1914, 649 pp.
[15] Holmes, Arthur, Petrographic Methods and Calculations. London, 1921, 515 pp.
[16] Weinschenk, Ernst, Petrographic Methods. New York, 1912, 396 pp.
[17] Clerici, Enrico ["Preparation of liquids for the separation of minerals"]: Rend. R. Accad. Lincei, vol. 16, sem. 1, ser. 5, 1907, pp. 187–195; Chem. Abs., vol. 1, pt. 2, 1907, p. 1371.

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of slightly amber hue, and extremely fluid. It can be diluted with water and reconcentrated. Seven grams each of formate and malonate dissolve in 1 c. c. of cold water. Ten grams of each leave some solid, and the filtrate has a specific gravity of 4.067 at 12° C. Formate alone gives this gravity only at 45° C. and malonate alone only at 60° C. By adding further quantities of the formate-malonate mixture, a specific gravity of 4.40 is reached at 35° and of about 4.65 at 50° C.

Clerici also worked out a substitute for the Thoulet solution. He found that 200 grams of $BaBr_2$+300 grams $HgBr_2$+90 grams H_2O give 180 c. c. of a colorless product having a specific gravity of 3.137 at 10° C.

Retgers made many experiments with heavy liquids to obtain one which would not attack sulphides. With acetates he obtained unsatisfactory results, the specific gravity seldom exceeding 4.0. The most satisfactory liquid was thallous acetate-nitrate ($TlAc.TlNO_3$), which melts at 65° C. and has a specific gravity of approximately 4.5. It is stable below 100° C. but rapidly decomposes at higher temperatures. The melting point of thallous acetate is 110° C.

Sodium metatungstate, with a specific gravity of 3.02, was the first heavy liquid used for the determination of the specific gravity of a mineral,[18] and sodium silicotungstate, with a specific gravity of 3.05, has also been used.

Retgers states that a saturated solution of SnI_4 in $AsBr_3$ has a specific gravity of 3.73 at 15° C. and a saturated solution of AsI_3+SbI_3 in a mixture of $AsBr_3$ and CH_2I_2 has a specific gravity of 3.7 at 20° C. These solutions, however, are opaque.

Retgers prepared a fluid of high specific gravity by slightly warming methylene iodide and dissolving in it as much idoform as it will take up. Usually some decomposition takes place and gives the solution a dark color. The solution when saturated and cold has a specific gravity of 3.6 to 3.65.

Retgers mentioned selenium monobromide (SeBr), which is a black semiopaque liquid with a specific gravity of 3.6 at 15° C. It has a disagreeable odor and tints the skin a permanent reddish brown. It is decomposed by heat, and with water it reacts to give selenium, selenious acid, and hydrobromic acid.

Retgers also states that a yellow oil-like fluid with a specific gravity of about 5.0 can be prepared by melting together $AgNO_3$ and AgI. The combination of the anhydrous salt is said to be $3AgI.2AgNO_3$. If AgI is in excess, the liquid is thick and useless.

[18] Karpinsky, A. ["Petrographische Notizen" (Iswestija des geol. Comites, III, Bd. 8, pp. 263–280), St. Petersburg, 1884]: Abs. in Neues Jahrb. Mineral., Geol., u. Paleont., Bd. 1, 1886, Referate, pp. 263–264.

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Breón[19] used lead chloride, which has a specific gravity of 5.0 and a melting point of 498° C., and zinc chloride, which has a specific gravity of 2.4 and a melting point of 262° C.; the two melt together in all proportions. The high melting point makes the melt practically useless.

F. I. du Pont[20] has described the use of $SnCl_4$, $SnBr_4$, and $SbBr_3$ for the separation of minerals from gangue. A. Nagelvoort[21] has described $SbBr_3$ and $AsBr_3$, and A. J. Moxam[22] has also described $SbBr_3$ for mineral separation.

DATA ON EXPERIMENTS—LIQUIDS TESTED

The purpose of this investigation was to obtain, if possible, better heavy liquids than those now employed and to learn more about their use. A liquid to be satisfactory should be cheap, easily prepared or obtainable, and transparent, have a low melting point, be noncorrosive to minerals, and be easily concentrated or diluted. These points were kept in the foreground during the entire investigation. Various liquids and molten salts were investigated and will be discussed in more or less detail.

RAPID METHOD OF DRYING

It is desirable and often necessary to have a dry mineral powder to work with. Some of the solutions to be described are decomposed by water. The presence of water changes the specific gravity of the solution if the solution is miscible with water; and if it is not miscible, the apparent specific gravity of the powder is changed. A rapid method of drying these particles has been devised. Acetone is a good solvent for water; it is nearly as volatile as ether, and it is relatively cheap. If the powder is put on a watch glass, or similar container, covered with acetone, and thoroughly wet by it, when the acetone is poured off the particles will dry in air in a couple of minutes. If the particles are rather fine and a watch glass can not be used, a wire-gauze basket can be substituted. The mesh of the basket

[19] Breón, M. R., "Séparation des minéraux microscopiques lourds": Soc. française mineral., Bull. 3, vol. 3, 1880, p. 46.

[20] du Pont, F. I., Process for the Liquid Separation of Solid Constituents: United States patent 994950, June 13, 1911; Gravity Liquid Separation of Certain Iron Ores: United States patent 1002865, Sept. 12, 1911; Liquid Gravity Separation of Solids: United States patent 1004815, Oct. 3, 1911; Liquid Ore Separation: United States patent 1014624, Jan. 9, 1912; Method of Gravity Liquid Separation of Solids: United States patent 1064459, June 10, 1913; Apparatus for Gravity Liquid Separation of Solids: United States patent 1067410, July 15, 1913; Process of Recovering Separating Liquids from Separated Solids: United States patent 1081949, Dec. 23, 1913; Apparatus for Liquid Separation of Solids: United States patent 1106195, Aug. 4, 1914.

[21] Nagelvoort, Adriaan, Process of Recovering Liquids Used for Separating Solids of Different Specific Gravities: United States patent 1244884, Oct. 30, 1917; Process of Separating Solids of Different Specific Gravities: United States patent 1244885, Oct. 30, 1917.

[22] Moxam, A. J., Ore Separating Process: United States patent 1151117, Aug. 24, 1915.

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should, of course, be finer than the particles of the powder. The powder is put into the basket and the mass is dipped into a beaker of acetone for a short time; then it is taken out and exposed to the air for a short time. A folded filter paper may also be used to hold the sample.

BROMOFORM—CARBON TETRACHLORIDE

Bromoform is a highly mobile liquid melting at 9° C. and boiling at 151.2°. The specific gravity of the pure material is 2.89 at 10° C.; commercial bromoform is seldom this heavy. The material used in this investigation had a specific gravity of 2.61 at 25° C. Once the bureau obtained commercial bromoform with a specific gravity of

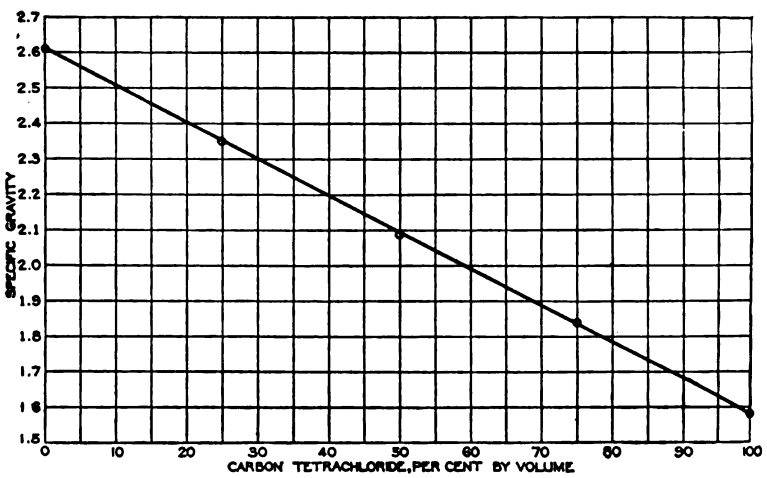

FIGURE 3.—Specific gravity of mixtures of bromoform and various proportions of carbon tetrachloride

2.86. Carbon tetrachloride and bromoform are miscible in all proportions. Carbon tetrachloride, a cheap organic solvent, has a specific gravity of 1.58, so a range in specific gravity from 1.58 to about 2.61 (or higher, depending on the purity of the $CHBr_3$) can be obtained. After separation has taken place the separated parts of the rock being examined can be washed with CCl_4, although removal of the last traces of bromoform from the mineral grains is rather difficult. The bromoform and the carbon tetrachloride can be recovered by fractional distillation. The low specific gravity of this solution restricts its use for the separation of heavy minerals from gangue, but it is satisfactory in separating coal from bone. Figure 3 and Table 2 give the specific gravity data for these two liquids.

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TABLE 2.—*Specific gravity of mixtures of CCl_4 and $CHBr_3$ at 25° C.*

Per cent $CHBr_3$ (by volume)	Specific gravity	Per cent $CHBr_3$ (by volume)	Specific gravity
100	2.61	25	1.84
75	2.35	0	1.58
50	2.09		

ACETYLENE TETRABROMIDE—CARBON TETRACHLORIDE

Acetylene tetrabromide melts at 0.13° C. and boils at 124 to 126° C. at 15 mm. Hg pressure. The liquid is colorless, mobile, and miscible

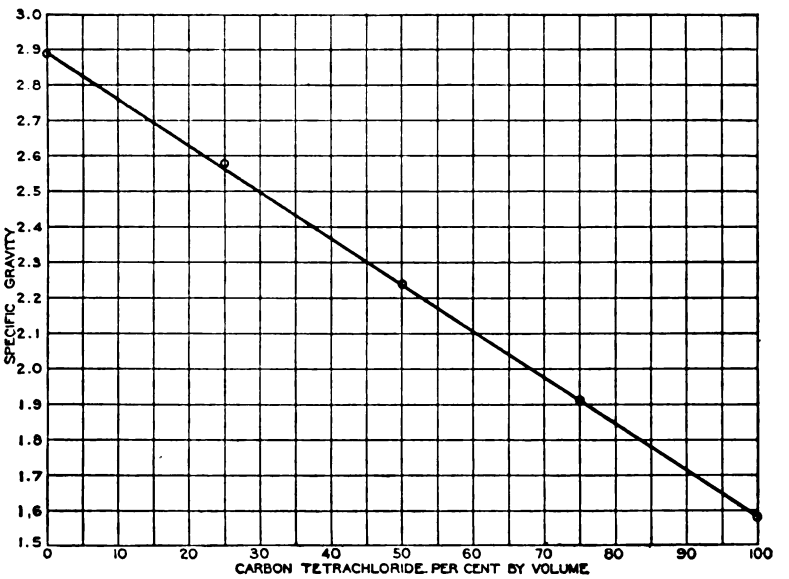

FIGURE 4.—Specific gravity of mixtures of acetylene tetrabromide and various proportions of carbon tetrachloride

with carbon tetrachloride in all proportions. The specific gravity of the pure liquid is 2.96 at 20° C.; the specific gravity of the commercial sample used in this investigation was 2.89 at 25° C. A range in specific gravity from 1.58 to 2.89 (or a little more) can be obtained by the use of this mixture. After separation of the particles of ore the particles of ore and gangue can be washed free with CCl_4 and the reagents recovered by fractional distillation. For more rapid washing benzene is better, and the acetylene tetrabromide may be recovered by fractional distillation. The specific gravity at 25° is given in Table 3 and Figure 4.

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TABLE 3.—*Specific gravity of mixtures of CCl_4 and $C_2H_2Br_4$ at 25° C.*

Per cent $C_2H_2Br_4$ (by volume)	Specific gravity	Per cent $C_2H_2Br_4$ (by volume)	Specific gravity
100	2.89	25	1.91
75	2.58	0	1.58
50	2.24		

The chemical and physical tables at hand did not furnish any data on the temperature coefficients of CCl_4, $CHBr_3$, and $C_2H_2Br_4$; so the specific gravity curve from 10 to 30° C. was determined. As the

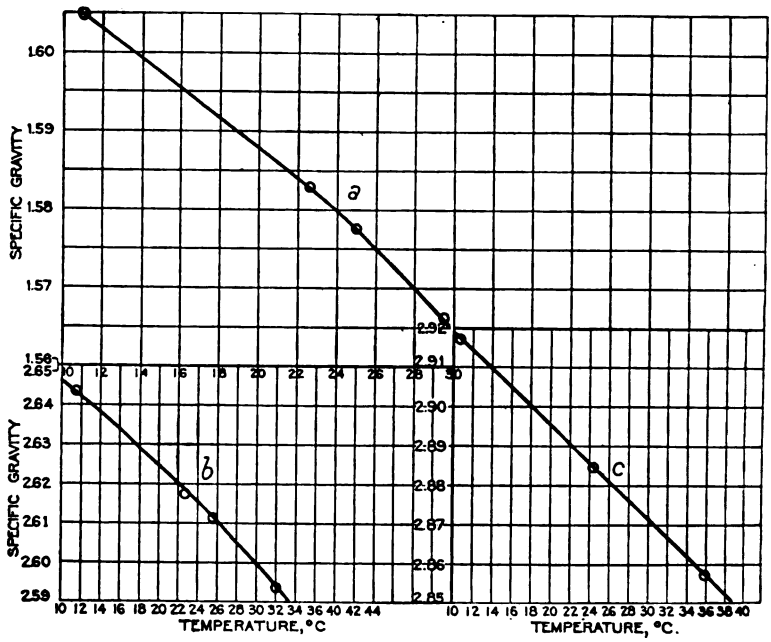

FIGURE 5.—Relations between temperature and specific gravity of carbon tetrachloride, bromoform, and acetylene tetrabromide: *a*, Carbon tetrachloride; *b*, bromoform; *c*, acetylene tetrabromide

materials will probably be used only at room temperatures, this was the only range studied. Figure 5 gives the data.

CARBON TETRABROMIDE—CARBON TETRACHLORIDE

Carbon tetrabromide is a white crystalline solid that melts at 92.5° C. and has a specific gravity of 3.42 in the solid state; when liquid it is miscible with carbon tetrachloride. Unfortunately, however, the specific gravity of melted tetrabromide is much lower, only 2.93 at 108° C. Thus the substance has no advantage over acetylene tetrabromide.

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STANNIC BROMIDE—CARBON TETRACHLORIDE

Stannic bromide melts at 30° C. to a colorless liquid that has a specific gravity of 3.35 at 35° C. The liquid has a low vapor pressure, and hence does not fume when exposed. Stannic bromide and CCl_4 are mutually soluble in all proportions in the liquid state; the mixture is molten at ordinary room temperatures except when the proportion of $SnBr_4$ approaches 100 per cent, and then even with pure $SnBr_4$ the melting point is not above 30° C. Specific gravities varying from 1.58 to 3.35 can be obtained by use of this mixture. The ordinary metallic sulphides PbS, Cu_2S, ZnS, FeS_2, and $CuFeS_2$ when dry are not attacked by it, but are attacked in the presence of water. Calcite in the dry state is not attacked; stibnite is acted upon slowly.

FIGURE 6.—Specific gravity of mixtures of stannic bromide and various proportions of carbon tetrachloride

After treatment the mineral particles can be washed free of $SnBr_4$ by means of CCl_4 and the salt recovered by evaporation or by fractional distillation. Messmore, working at the Mississippi Valley station of the Bureau of Mines, found that if the stannic bromide was not protected with a drying tube on a humid day it absorbed moisture from the air and formed gummy, sticky masses on the edge of the vessel in which the separation was taking place and on the mineral particles themselves. Carbon tetrachloride does not dissolve this gummy compound. Water or ether dissolves it easily, but, of course, if it is dissolved in water, the stannic bromide is lost.

The stannic bromide prepared in this investigation had a specific gravity of 3.334 at 35° C. Table 4 and Figure 6 give the specific gravity data for mixtures of $SnBr_4$ and CCl_4.

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TABLE 4.—*Specific gravity of mixtures of $SnBr_4$ and CCl_4 at different temperatures*

Per cent $SnBr_4$ (by weight)	Specific gravity	Temperature (°C.)	Per cent $SnBr_4$ (by weight)	Specific gravity	Temperature (°C.)
100	3.334	35.0	32.5	1.91	24.0
73	2.58	22.3	0	1.58	25.0
49.5	2.14	23.0			

Since stannic bromide is of value for use as a heavy liquid, a method for its preparation is given.

Put powdered tin or pieces of tin 2 to 3 cm. long into a distilling flask. Connect a water-cooled reflux condenser to the flask and let in dry bromine drop by drop through the top of the condenser. Fit a $CaCl_2$ drying tube to the end of the distilling tube to prevent moisture from reaching the interacting substances. The heat of reaction is sufficient to make the action vigorous, hence the reflux condenser is necessary to prevent the loss of bromine. After the action is completed the reflux condenser is removed and a one-hole stopper carrying a thermometer is put in its place. Heating drives off any excess bromine, and the bromide can be distilled into a dry container. A splendid snow-white crystalline mass is obtained. Melting point, 30° C.; boiling point, 203° C.

STANNIC CHLORIDE

Stannic chloride melts at —33° C., boils at 114° C., and has a specific gravity of 2.2788 at 0° C. The salt, prepared by direct chlorination, was found to be mutually soluble in all proportions with $SnBr_4$. As it has a high vapor pressure and suffocating odor, its value was deemed slight.

STANNIC IODIDE

Stannic iodide prepared had a specific gravity of about 3.55 at 150° C. Its high melting point and very dark color prevent it from being a satisfactory heavy liquid.

ANTIMONY TRIBROMIDE

The same method of preparation is used for antimony tribromide as for tin tetrabromide. Caution is necessary, however, as bromine and antimony unite vigorously with the evolution of heat and light; hence the bromine must be added slowly, drop by drop. Antimony tribromide melts at 94.2° and boils at 280° C. In the liquid state the salt is mutually soluble in all proportions with stannic bromide, and specific gravities ranging from 3.11 to 3.65 may be obtained from a mixture of the two at 108° C. $SbBr_3$ is soluble in

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absolute alcohol, acetone, bromoform, and carbon bisulphide, and can be washed from the minerals with these reagents. It is to be noted, however, that 95 per cent alcohol and some technical grades of acetone are not suitable for this work, as they contain enough water to hydrolyze the salt and precipitate the oxychloride. Table 5 and Figure 7 give the specific gravity data for mixtures of $SnBr_4$ and $SbBr_3$.

TABLE 5.—*Specific gravity of mixtures of $SnBr_4$ and $SbBr_3$*

Per cent $SbBr_3$ (by weight)	Specific gravity	Temperature (° C)	F. P.	Per cent $SbBr_3$ (by weight)	Specific gravity	Temperature (° C.)	F. P.
100	3.64	108	94.2	24.8	3.26	108	71
72.2	3.45	108	82	0	3.11	108	30
50.8	3.38	107	77				

It is to be noted that the measurements were made at a temperature of 108°, or about 14° above the melting point of pure $SbBr_3$. A

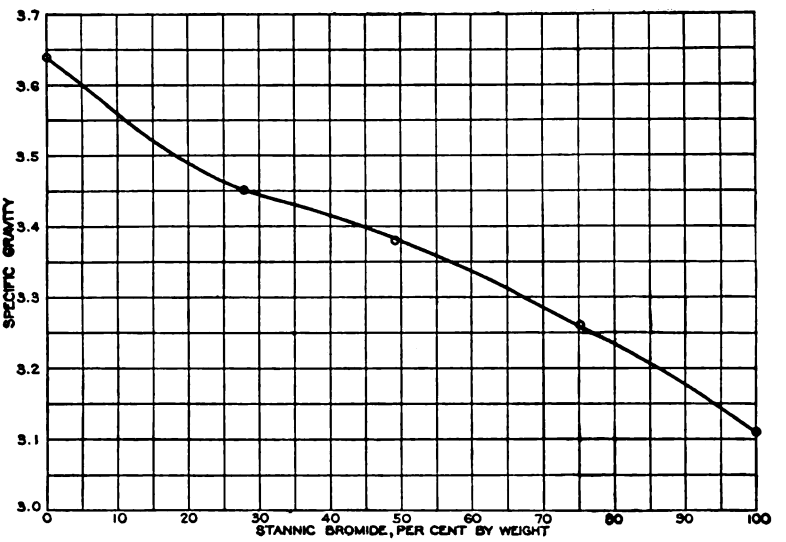

FIGURE 7.—Specific gravity of mixtures of antimony and various proportions of stannic bromide

gravity higher than this could be obtained by maintaining a lower temperature—say, 5 to 10° above the melting point of the mixture. Also, inasmuch as the highest melting point of the series is 94.2° C., the mixture can be easily kept molten on a steam bath.

ANTIMONY TRIBROMIDE—BROMOFORM

Antimony tribromide and bromoform are miscible in the liquid state. A range of specific gravity from 2.6 to 3.65 can be obtained

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with a mixture of these liquids. Table 6 and Figure 8 give the data. When antimony tribromide and bromoform are heated for some time to about the melting point of antimony tribromide or a little higher, the liquid acquires an opaque red color and has a sharp stinging odor.

TABLE 6.—*Specific gravity of mixtures of $SbBr_3$ and $CHBr_3$*

Per cent $CHBr_3$ (by weight)	Specific gravity	Temperature (° C.)	Per cent $CHBr_3$ (by weight)	Specific gravity	Temperature (°C.)
100	2.49	77	25	3.32	80
75	2.72	82	0	3.64	94.2
50	3.00	80			

After treatment the minerals can be washed with CS_2 and the heavy liquids recovered by fractional distillation.

An attempt was made to increase the density by dissolving various salts in $SbBr_3$. In a few mixtures a slightly higher specific gravity

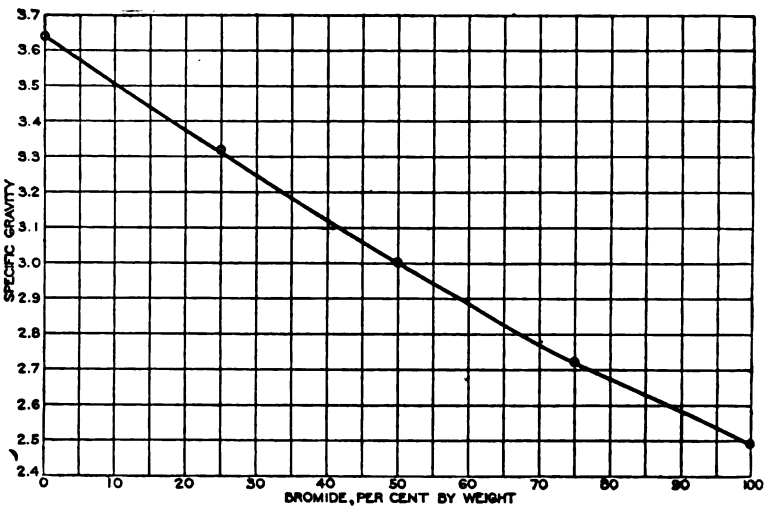

FIGURE 8.—Specific gravity of mixtures of antimony tribromide and various proportions of bromoform

was obtained, but this increase was accompanied by an increase in the melting point. By heating $SbBr_3$ with an excess of HgCl until the solution was saturated with the latter the specific gravity was increased to 3.9 at 150° C., but the melting point was very close to 150° C. A mixture containing 30 molecular per cent of $SbBr_3$+70 molecular per cent of SbI_3 is molten at the temperature of the water bath and has a specific gravity of 3.89. The large amount of the iodide present renders the mixture very opaque.

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ANTIMONY TRICHLORIDE

Antimony trichloride can be prepared either by a "wet" or "dry" method. The sample used in this investigation was prepared by a "wet" method, as follows: Dissolve Sb_2O_3 in hydrochloric acid, transfer to a distilling flask, and heat. Boil off the water and then the excess hydrochloric acid. Before all the acid is driven off, pass a stream of dry HCl gas, made by the action of H_2SO_4 on dry NH_4Cl, through the solution. After the excess of HCl is boiled off, raise the temperature and distill the antimony trichloride. Redistill in a stream of dry HCl gas. Put the salt under vacuum and remove the last traces of the HCl.

In the "dry" method the anhydrous salt is produced by passing chlorine gas through powdered antimony covered with a little antimony trichloride. The anhydrous salt is then distilled into a dry container.

Pure $SbCl_3$ melts at 73.2° C. and boils at 223.5° C. It is mutually soluble in all proportions with antimony tribromide. Properties similar to those of the bromide may be attributed to the chloride. Dry metallic sulphides are not attacked by the anhydrous salt.

The sample prepared and used in this investigation had a specific gravity of 2.59 at 100° C. Table 7 and Figure 9 give data on the specific gravities of the mixtures used in this investigation.

TABLE 7.—*Specific gravity of mixtures of $SbBr_3$ and $SbCl_3$*

Per cent $SbCl_3$ (by weight)	Specific gravity	Temperature (° C.)	F. P.	Per cent $SbCl_3$ (by weight)	Specific gravity	Temperature (° C.)	F. P.
100	2.59	100	70.8	36.5	3.18	101	60.5
59.9	2.92	100	60.6	0	3.64	108	94.2

The specific gravity, at 65° C., of a mixture of 59.9 per cent $SbCl_3$ with 40.1 per cent $SbBr_3$ was 3.156. Any mixture of the two salts can be kept molten on the steam bath.

To determine whether these halogen salts would attack the water of crystallization in mineral substances, samples of dry kaolinite and muscovite were treated with $SnBr_4$ and $SbBr_3$. No action resulted from the $SnBr_4$ in either test, but about 0.5 per cent of the weight of the kaolinite and about 2 per cent of the weight of the muscovite were lost after treatment with $SbBr_3$.

THALLOUS SILVER NITRATE

Thallous nitrate was prepared by the action of nitric acid on thallium. The solution was evaporated until the salt began to crys-

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tallize out in the hot solution. After it had cooled the mother liquor was decanted and further concentrated. The salt was dissolved and recrystallized. Equal molecular parts of dry $TlNO_3$ and dry $AgNO_3$ were heated; the mixture melted at 74° C. The gravity of the mixture at 75° C. was 4.64. A quantity of tallous nitrate was prepared by dissolving thallium in nitric acid and precipitating the $TlNO_3$ by adding C_2H_5OH. When equal molecular parts of this salt and $AgNO_3$ were melted together, a partial decomposition of the melt took place and white crystals floated to the top. Probably some organic compound of thallium was formed which remained with the thallium nitrate and decomposed on heating.

Thallous silver nitrate forms a highly mobile, colorless liquid and may be satisfactory for many separations, but it is unsatisfactory

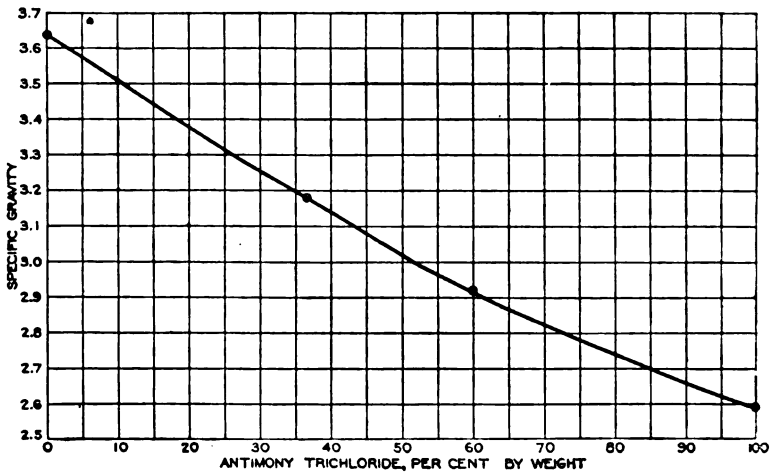

FIGURE 9.—Specific gravity of mixtures of antimony tribromide with various proportions of antimony trichloride

for sulphides because of the silver salt. The melt can be diluted by slowly adding hot water to it while stirring it, and the solution again concentrated by evaporation. The addition of water also lowers the melting point. C. O. Anderson, metallurgist of the Bureau of Mines, told the author that the melting point of the solution with a specific gravity of 4.2 is 66° C.

A range in specific gravity from 1.0 to about 4.6 can be obtained by the use of thallous silver nitrate and water. The two salts may be recovered through the insolubility of the chlorides. Addition of hydrochloric acid or a solution of a chloride precipitates TlCl and AgCl, which can be converted back into the nitrate by means of HNO_3. Also Ag^+ is precipitated in acid solution by H_2S, but Tl^+ is not; hence the two salts can be separated. Furthermore, Ag^+ can be precipitated by KOH, whereas the thallium remains in solu-

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tion because of the solubility of the hydroxide. Thus the two metals can be separated and after the separation be converted back to the nitrates. A quantitative separation may be brought about by passing chlorine through a solution containing the two salts. The silver is precipitated as the chloride, but the thallium is oxidized to the "ic" condition, leaving $TlCl_3$ in solution.

MERCUROUS NITRATE

Mercurous nitrate ($HgNO_3.1H_2O$) is said to melt at 70° C. and to have a gravity of 4.3. When Hg is dissolved in dilute HNO_3, mercurous nitrate forms, but the salt formed by the action crystallizes with varying amounts of water; these amounts depend on the temperature and the concentration of free acid present. Therefore it is rather difficult to get a pure sample of $HgNO_3.1H_2O$. A sample of wet mercurous nitrate was dried in a vacuum desiccator over P_2O_5 (the drying takes place rapidly) until the specific gravity of the molten salt was found to be 4.3 at 85° C.

Mercurous nitrate is unsatisfactory as a separating medium. The salt decomposes rapidly near the boiling point of water, and even at lower temperatures, to a basic nitrate. If enough HNO_3 is added to prevent decomposition or to convert the basic nitrate to the normal nitrate after decomposition has started, enough free acid is present to attack sulphides. The molten salt can be diluted with a little water, but the addition of excess water causes precipitation of a basic nitrate and finally of mercuric oxide, if the dilution is carried far enough. If HNO_3 is added to prevent the hydrolysis, the concentration of acid becomes sufficient to decompose sulphides. The melt is very mobile, however, and in the separation of large particles, which takes place rapidly, it may find some use.

THALLOUS MERCUROUS NITRATE

Thallous mercurous nitrate is said to have a specific gravity of 5.3, but the author of this paper obtained no such result. When equal molecular parts of $TlNO_3$ and $HgNO_3.1H_2O$ (specific gravity, 4.3) were melted together, the specific gravity of the resulting melt was about 4.7. When one remembers that the specific gravity of thallous nitrate at its melting point is only 4.94, it does not seem logical to expect that adding equal molecular parts of a material with a specific gravity of 4.3 will increase the specific gravity of the resulting mass to 5.3. Pure dry desiccated $HgNO_3$ added in equal molecular parts to $TlNO_3$ decomposed without melting.

Thallous mercurous nitrate is much more stable than mercurous nitrate itself. A melt did not decompose for several hours when maintained near the boiling point of water. Addition of a small

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amount of nitric acid further arrests decomposition, and tests showed that such a solution attacks chalcocite but slightly after a day. When diluted the melt is not hydrolyzed by a small amount of water, but decomposition takes place if much water is added.

As both TlCl and HgCl are insoluble, the two nitrates can be recovered by adding hydrochloric acid or a soluble chloride and converting the chlorides formed to nitrates by treating them with HNO_3.

THALLIUM FORMATE

Cost is an item in the determination of the liquid to be used. Thallous silver nitrate is a fairly satisfactory liquid for a range in density of 3.65 to 4.6, if no sulphide particles are present. Thallium can be purchased for about $5 a pound, whereas silver is much higher—more than $10 a pound. Tests have showed that thallous formate will cover more than the specific gravity range given by the thallous silver nitrate melt; and as thallium is cheaper than silver, the formate is preferable to the mixed nitrates. The formate is superior to the double nitrate in some other respects; it can be used when sulphides are present, whereas the fused nitrates can not.

The formate was prepared by treating the sulphate with an equivalent quantity of $Ba(OH)_2$, which gives insoluble $BaSO_4$ and soluble TlOH. The hydrate solution, when filtered, was evaporated to a small volume, formic acid was added, and the solution evaporated to dryness. Then the salt was dried in a vacuum desiccator over P_2O_5. Thallous formate may also be prepared by adding a barium formate solution to a thallous sulphate solution. Experiments showed that when an ammoniacal solution of thallous nitrate was treated with H_2S to precipitate Tl_2S and the sulphite dissolved in formic acid to form $TlCO_2H$, the resulting formate contained ammonium salts which decomposed upon heating, sometimes even with explosive violence. Clerici stated that the formate is best prepared from the carbonate, which he made as follows: Metallic thallium was broken into small pieces; these were beaten into sheets which were rolled up like shavings. The rolled sheets were placed in an open vessel with not enough water to cover them; after a day water was added, heat was applied, the solution was filtered, and allowed to crystallize. These operations were repeated until the metal was all exhausted. The method is tedious. The free organic acids react very slowly on the metal.

The thallium formate made melted at 94° C. and had a specific gravity of about 4.95 at 105° C. It is very soluble in water, and its solubility increases rapidly with increasing temperature. A mixture of 5 per cent H_2O with 95 per cent $TlCO_2H$ melts at 54° C. and has a specific gravity of 4.19 at 60° C.; 10 per cent H_2O with 90 per cent

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$TlCO_2H$ melts at 31° C. and has a specific gravity of 3.72 at 42° C.; 15 per cent H_2O with 85 per cent $TlCO_2H$ is molten at 22° C. and has a specific gravity of 3.39 at 25° C.; 20 per cent H_2O with 80 per cent $TlCO_2H$ has a specific gravity of 3.09 at 25° C.; 25 per cent H_2O with 75 per cent $TlCO_2H$ has a specific gravity of 2.86 at 25° C. The data appear in Figure 10. The salt does not decompose at the temperature of boiling water, but decomposes slowly at a slightly higher temperature. The solution of thallous formate can be concentrated by evaporation. A comparison of the experimental data on thallous formate with the data obtained by Clerici (see p. 7) shows that the results check. The malonate salt of Clerici was not investigated, but as his work on the formate was checked his work on the malonate is accepted.

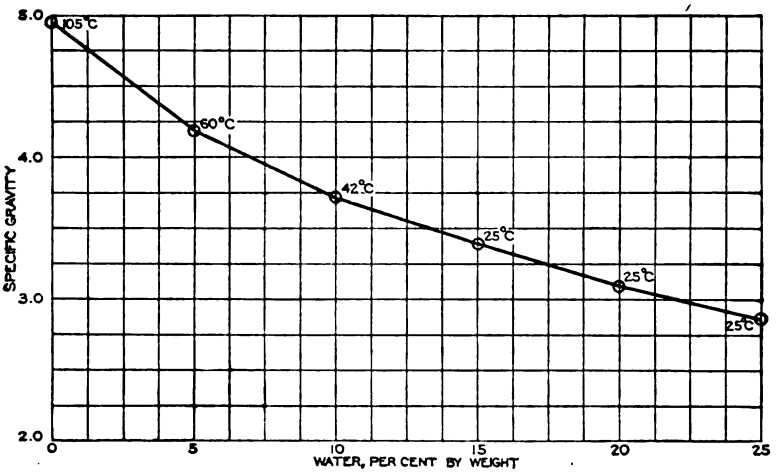

FIGURE 10.—Specific gravity of solution of thallous formate

It was hoped that the formate of some cheaper heavy metal than thallium might be substituted, but none that answered the purpose could be found. Lead formate decomposes at 190° without melting and is virtually insoluble in water. Mercurous formate decomposes without melting and is decomposed by water. Barium formate is virtually insoluble, whereas nickel formate decomposes without melting. The acetates of the heavy metals were found to be unsatisfactory.

MERCURIC CHLORIDE—MERCURIC IODIDE—ANTIMONY TRICHLORIDE

Mercuric chloride and mercuric iodide form an eutectic that contains 47 per cent (molecular) of the iodide and melts at 145° C.[23] Equal molecular parts were weighed out, and it was found that the

[23] Landolt-Börnstein, Physikalisch-Chemische Tabellen. Berlin, 1923, p. 616.

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molten mass had a specific gravity of 5.2 at 150° C. $SbCl_3$ proved to be miscible in all proportions in the liquid state with this 50–50 mixture. Tests showed that 1 part of the mixture to 1 part $SbCl_3$ had a specific gravity of 3.44 at 121° C., and 3 parts mixture to 1 part $SbCl_3$ had a specific gravity of 4.05 at 145°, while 87.5 per cent of the mixture and 12.5 per cent $SbCl_3$ had a specific gravity of 4.55 at 135° C.

All three components are soluble in aniline oil, and aniline is miscible in all proportions with ether and alcohol. The mineral particles can be freed from the melt by dissolving the heavy solution (or the solidified salt after cooling) with aniline and then freed from aniline by means of alcohol or ether.

This melt decomposes sulphides, but may be valuable for separating nonsulphide minerals when a liquid of high specific gravity is required. The melt is dark but not entirely opaque.

AMALGAMS

Sodium amalgams containing 20 molecular per cent to 100 molecular per cent of sodium are molten at a temperature less than 100° C.[24] It was thought that possibly a series of heavier liquids could be thus produced, but the sodium amalgams proved unsatisfactory because of their reactivity. Iron oxides were readily decomposed by an amalgam.

Gallium.—Metallic gallium is a melt that is of interest, although probably not practical. The metal melts at about 30° C., and according to Richards and Boyer[25] has a specific gravity of 6.08 in the liquid state. J. W. Mellor[26] says that L. de Boisbaudran found that gallium alloys readily with aluminum, and mixtures rich in gallium are liquid at ordinary temperatures. It is altogether possible that a series with gravities ranging from 4.95 ($TlCO_2H$) to 6.08, liquid at ordinary temperatures, could be obtained by suitable proportions of Ga and Al. As Ga is scarce and high priced, the liquid is not considered feasible now, but may possibly be utilized.

COLLOIDS

The possibility of using heavy colloidal solutions has been suggested, but colloidal solutions of a high specific gravity are not liquid. About 2 or 3 per cent of metal causes the metallic colloids to become butterlike.

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[24] Landolt-Börnstein, Physikalisch-Chemische Tabellen. Berlin, 1923, p. 569.

[25] Richards, T. W., and Boyer, Sylvester, "Further studies concerning gallium. Its electrolytic behavior, purification, melting point, density, coefficient of expansion, compressibility, surface tension, and latent heat of fusion": Jour. Am. Chem. Soc., vol. 43, pt. 1, 1921, pp. 274–294; "The purification of gallium by electrolysis and the compressibility and density of gallium": Jour. Am. Chem. Soc., vol. 41, pt. 1, 1919, p. 133.

[26] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry. London, 1924, vol. 5, p. 380.

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Much study was done in search of other suitable liquids, but none with high specific gravities were found. Landolt's tables were combed through, and many other handbooks, journal articles, and books were studied, but nothing further of value has come to light.

COMPARISON OF DENSITY OF MINERALS BY THE SINK-AND-FLOAT METHOD AND WITH THE PYCNOMETER

It is desirable to know the specific gravity of a liquid that will float or sink a mineral specimen of known specific gravity. The specific gravities of liquids have often been determined by finding a mineral that is just on the border line between sinking or floating. The specific gravity of minerals has also been determined by finding a liquid mixture that will just suspend the mineral particles and then determining the specific gravity of the liquid by one of the well-known methods. The specific gravities of several minerals were determined by means of a pycnometer, and then some of the mineral particles were put into various solutions of heavy liquids and the specific gravity of the liquid which would cause a floating particle to sink, or a sunk particle to float, was determined. Ottawa standard sand, 20 to 30 mesh, with a specific gravity of 2.69, when suspended in a mixture of CCl_4 and $C_2H_2Br_4$ of the same specific gravity floated and did not sink until the specific gravity of the solution was decreased, by the addition of small amounts of CCl_4, to 2.64. It did not sink in a mixture of $CHBr_3$ and CCl_4 until the specific gravity was decreased to 2.64. In a thallous formate solution the sand sank when the specific gravity of the solution was decreased to 2.63. In the same solutions 20 to 30 mesh calcite, specific gravity 2.75, would not sink until the specific gravity of the solutions was reduced to 2.72, 2.71, and 2.71, respectively. Alundum (60 mesh) of a specific gravity of 3.92 would not sink in a thallous formate solution until the specific gravity was reduced to 3.86. All the minerals tested were nonporous; more porous minerals would show a greater deviation from their true specific gravity.

Although the sink-and-float method is not accurate enough for the scientific determination of the specific gravities of minerals, it is accurate enough for certain purposes, such as ore-dressing work, of which fractionation is the aim.

Clerici[27] measured the viscosity of 16 of the liquids ordinarily used in mineral separation and plotted the viscosity against the specific gravity. Klein's solution had the highest viscosity. For a specific gravity of 2.88, $CHBr_3$ had the lowest viscosity, thallous formate, thallous malonate, Clerici's $BaBr_2+HgBr_2$ increased in the order given. The viscosity of the Clerici thallous formate-malonate

[27] Clerici, Enrico ["Viscosity of liquids for the mechanical separation of minerals"]: Rend. R. Accad. Lincei, vol. 20, sem. 1, ser. 5, 1911, pp. 45–50; Chem. Abs., vol. 5, pt. 2, 1911, p. 2058.

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liquid increased slowly up to a specific gravity of 3.5 and then more rapidly, but even at a specific gravity of 3.7 the viscosity was less than that of any other liquid of that gravity.

It is to be noted that when a melt is composed of two components of different vapor pressures, the component with the higher vapor pressure will evaporate more rapidly than the component of lesser vapor pressure. In the process of evaporation the resulting solution becomes enriched with one component, and in consequence the specific gravity of the solution changes. This change in specific gravity due to evaporation is especially noticeable at higher temperatures. If a sink-and-float separation is carried on over a long period of time, the specific gravity of the solution may have to be adjusted by adding some of one component of the solution. This also emphasizes the desirability of choosing a melt so mobile that rapid separation is possible.

This investigation has shown what seem to be the best liquids to use at different specific gravity ranges. The price of the reagent, its fluidity, transparency, ease of preparation and recovery, and ease of handling have been taken into account. Based on the experience gained in this research and the foregoing considerations, the liquids named in the table that follows are recommended for their respective ranges of specific gravity.

TABLE 8.—*Heavy liquids recommended*

Density range desired	Heavy liquid recommended	Reagent to clean particles from heavy liquid	Remarks
1.58 to 2.6	Bromoform+carbon tetrachloride.	Carbon tetrachloride	Liquid at ordinary room temperatures; reagents recovered by fractional distillation.
2.6 to 2.9	Acetylene tetrabromide + carbon tetrachloride.	Carbon tetrachloride, benzene.	Do.
2.9 to 3.3	Stannic bromide+carbon tetrachloride.	Carbon tetrachloride	Molten at 30° when pure $SnBr_4$ is used, but with small addition of CCl_4 is molten at room temperatures; mineral particles must be dry to prevent decomposition of melt; reagents recovered by fractional distillation.
3.3 to 3.65	Antimony tribromide+stannic bromide.	Carbon bisulphide, absolute alcohol, bromoform, or absolute acetone.	Molten on steam or water bath; mineral particles must be dry; recovered by fractional distillation.
3.65 to 4.95	Thallium formate+H_2O[1]	Water	Water or steam bath will keep mass molten over entire range; reagent recovered by evaporation.
4.95 to 5.2	Eutectic of $HgCl_2$ and HgI_2+antimony trichloride.	Aniline followed by alcohol or ether.	Molten on oil bath; can not be used when sulphides are present.

[1] The Clerici thallous formate malonate can be substituted for the formate except at the highest range of density. The prime difference between the two is that the mixture melts at a lower temperature for the same density. The malonate is more expensive than the formate.

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ADDENDUM

After more than two years' work on the separation of minerals by means of heavy liquids, H. E. Messmore, W. H. Coghill, and C. O. Anderson, using the above-described solutions and methods at the Mississippi Valley Station of the Bureau of Mines, have simplified their practice to and adopted the following procedure:

For the laboratory study of ores, only two heavy liquids are usually necessary. Acetylene tetrabromide is recommended for all low-gravity work. Many ores contain quartz or calcite as gangue, and acetylene tetrabromide has a high enough gravity to float free a gangue composed of either of these minerals. As many ores contain more gangue than valuable minerals, the use of acetylene tetrabromide is recommended because it will remove the larger part of the sample; the smaller remaining part may then be treated with a more expensive, heavier liquid.

The most suitable liquid for sink-and-float work on minerals of high specific gravity is a water solution of the double thallous formate-malonate. This double salt, with a specific gravity of 4.9, melts at 60° C. and is miscible in all proportions with water. At room temperatures the salt is soluble enough to give a solution with a specific gravity of nearly 4.3. As a liquid of intermediate gravity, an aqueous solution of thallous formate is recommended. It is less expensive than the formate-malonate. A maximum specific gravity of about 3.5 is reached at room temperatures, and gravities up to 4.95, the gravity of the molten salt, may be obtained.

Messmore has avoided the use of the halogens, stannic bromide, and antimony tribromide because of the added care and precautions necessary in their use. Stannic bromide hydrolyzes in moist air, and if the separation requires a long period of time with the solution standing open to the air a gummy mass forms on the container; consequently the separation must be made in the absence of moisture. A drying tube must be attached to the mouth of the container.

Because of cheapness and desirable properties acetylene tetrabromide diluted with carbon tetrachloride is recommended for gravities of 2.95 and below; because of its cheapness compared with the malonate-formate thallous formate solution is recommended for gravities from 2.95 to 3.5; and the malonate-formate solution is recommended for gravities above 3.5.

Heavy liquids recommended by Messmore

Range of specific gravity	Heavy liquid	Diluting or washing reagent	Recovery of heavy liquid
1.6 to 2.95	Acetylene tetrabromide	Chloroform or benzene	Evaporation or fractional distillation.
2.95 to 3.5	Thallous formate	Water	Evaporation on steam bath.
3.5 to 4.9	Thallous formate-malonate	do	Do.

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Messmore, Coghill, and Anderson also arrived at the conclusion that cheapness of solution is not as big an item as they had anticipated before beginning work with heavy liquids. They believe that the benefit gained by the use of heavy liquids is great enough to justify buying a pint or two of the more expensive liquids, which are easy to handle and aid in rapid separation of the mineral increments.

More recently one of the bureau metallurgists, W. H. Coghill, has published a study [28] of the Alabama red iron ores, which reported the use of heavy liquids for separation of the various minerals. The method described is an excellent example of the use of these liquids in connection with ore dressing.

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[28] Coghill, W. H., Degree of Liberation of Minerals in the Alabama Low-Grade Red Iron Ores After Grinding: Reprint No. 1616–B, Trans. Am. Inst. Min. & Met. Eng., February, 1927, meeting.

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